

Gas phase photocatalysis and liquid phase photocatalysis: Interdependence and influence of substrate concentration and photon flow on degradation reaction kinetics

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Abstract

The photocatalytic degradation of metolachlor in water and butyric acid in air on coated TiO₂ has been investigated to study the interdependency on the degradation rate of the UV photon flux and the concentration of the organic compound. Experimental results clearly showed that the kinetic change of order with respect to light intensity depended on the value of the concentration of organic compound. The fitting of experimental results with the Langmuir–Hinshelwood (L-H) model emphasized that the corresponding “apparent adsorption constant”, K_R , could not be considered as an equilibrium constant in the dark since the value of K_R varied with regard to the photon flow. The assumption of a pseudo-steady-state for the concentration of hydroxyl radicals associated either with L-H model (under certain conditions) or Eley–Rideal model explains consistently the dependence of the apparent kinetic parameter, k_{obs} , and K_R with the light intensity. A rate expression taking into account the interdependency of the degradation rate on the UV photon flux and the initial concentration of the organic compound is proposed and validated for a liquid and a gas phase reaction. The constants of this correlation are independent of the initial concentration and light intensity.

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1. Introduction

The heterogeneous photocatalytic process is a suitable technique for degrading organic water and air pollutants. As an example, many pesticides or dyes can be partially or completely mineralized [1–3] in water and odorous compounds can be destroyed in gas phase [4,5]. During the photocatalytic process the catalyst is activated by photons. When the semiconductor, TiO₂, is irradiated with photons of appropriate energy (UV), the formation of an electron–hole pair occurs, and then these charges can either recombine or participate in different reactions. Many studies have focused on the chemical pathways or on the degradation kinetics, but there have been few reports based on the design of photocatalytic reactors, among them we can cite [6–9]. It is necessary to have a better knowledge of the

optimal photocatalytic process conditions. The challenge of photocatalysis consists in designing reactors with increasing efficiency. For this goal, it is important to have a better understanding of the influence of concentration and light intensity on the degradation rate. The dependency of the degradation rate on the concentrations is widely reported by means of the Langmuir–Hinshelwood (L-H) model in a batch reactor for a given light intensity combined with the assumption that the oxygen is adsorbed on different adsorption sites than the other products [10–12]:

$$r = -\frac{dC_R}{dt} = k' \frac{K_R C_R}{1 + K_R C_R + \sum_i K_i C_i} \frac{K_{O_2} C_{O_2}}{1 + K_{O_2} C_{O_2}} \quad (1)$$

where k' is a kinetic parameter, K , K_i and K_{O_2} are the adsorption parameters of the target compound, by-products and oxygen, respectively, depending on the compound and the catalyst. C_R , C_i and C_{O_2} are the concentration of the target compound, the by-products and the oxygen, respectively. The values of the

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adsorption parameters depend on the experimental conditions such as the temperature, the solution pH, the ionic strength, etc. In many cases, the expression (1) is simplified by including the surface coverage of oxygen in an apparent kinetic parameter and by considering the initial degradation rate. Indeed, the last assumption allows neglecting the $\sum_i K_i C_i$ term which is difficult to estimate because all the major intermediates and by-products must have been identified, their adsorption parameters and own degradation kinetic parameter evaluated and their mass balance included in the calculations. So, expression (1) becomes expression (1a):

$$r_0 = \frac{k_{\text{obs}} K_R C_R}{1 + K_R C_R} \quad (1a)$$

where k_{obs} is an apparent kinetic parameter depending on light intensity, mass and nature of the catalyst, and concentration of the electron carrier (O_2 and H_2O_2). For low concentration, $K_R C_R \ll 1$, Eq. (1a) reduces into $r_0 = k_{\text{obs}} C_R$, for high concentration $K_R C_R \gg 1$, the degradation rate is maximal and of order 0 with regard to the initial concentration [13]. This expression is only valid at the beginning of the reaction when the by-products are produced in a negligible amount.

The dependency of the degradation rate with the photon flux is linked to the activation of the catalyst as previously mentioned. A power law relation is often used (2) [14]

$$r \propto I^n \quad (2)$$

For the low light intensities, the degradation rate is linear with the photon flux ($n = 1$), for an increasing value of photon flux the degradation rate is modeled proportionally to the square root ($n = 1/2$). This transition is explained by Ollis et al. [14] and Kormann et al. [15] as a consequence of the predominant recombination of electron–hole pairs versus the charge transfer. For the higher light intensities, the order of the reaction is 0 with regard to the light intensity ($n = 0$); the mass transfer of the organic compounds to the catalyst surface is the limiting parameter.

The simplified L-H expression (1a) has been originally proposed, using the assumption of a slow rate-controlling surface step as shown by the equations below:



Considering the Langmuir expression of the surface coverage, θ_R :

$$\theta_R = \frac{K_R C_R}{1 + K_R C_R} \quad (5)$$

The rate expression is then given by $r = k_{\text{obs}} \theta_R$ which is equivalent to Eq. (1a). In Eq. (5), the parameter K_R is the Langmuir constant $K = k_1/k_{-1}$ which refers to the adsorption/desorption equilibrium and is supposed to be independent of the light intensity during photocatalytic reaction. Nevertheless, some authors have described the influence of the photon flow

on both the L-H kinetic parameter (k_{obs}) and the apparent adsorption/desorption parameter (K_R). It was based on experimental evidences observed during photocatalytic degradation of phenol [16], acetophenone [17] and methylviologen [18], all of them in the liquid phase. Up to day, such experimental evidence has not yet been reported in the gas phase.

Ollis [19] and Emeline et al. [16] both proposed to use a pseudo-steady-state analysis to explain the intensity dependence of the L-H kinetic parameter and the apparent adsorption parameter. Ollis [19] used the pseudo-steady-state hypothesis applied to the surface coverage of reactant, θ_R , and Emeline et al. [16] used the pseudo-steady-state hypothesis for the concentration of hydroxyl radical. These two approaches concluded that the apparent equilibrium parameter in the L-H model cannot be considered as an adsorption equilibrium constant in the dark. However, the quasi-steady-state approximation on the surface coverage failed to explain the experimental result that showed that K_R (under irradiation) is superior to the adsorption equilibrium constant in the dark.

Surprisingly, many studies have been focused on the dependencies of the kinetic either on the initial concentration at a given photon flux or on the photon flux at a given initial concentration, but only few papers deal with the interdependence of the degradation rate on the initial concentration and the light intensity in liquid and gas phase. A kinetic expression considering the concentration of the compound and the light intensity has been proposed by Emeline et al. [16]:

$$r(C_R, I) = \frac{\beta I C_R}{\gamma I + \chi C_R} \quad (6)$$

where β , γ and χ are independent of the initial concentration and the light intensity. On the other hand, the previous authors showed that expression (7) could be consistently used to highlight the interdependence of the concentration and the photon flow on the reaction rate. They indicated that orders m and n are interdependent since, in accordance with their experimental results, $m \rightarrow 1$ when $n \rightarrow 0$ and $n \rightarrow 1$ when $m \rightarrow 0$.

$$r(C_R, I) = k'_{\text{obs}} C_R^m I^n \quad (7)$$

The aim of this paper is:

- To study the light intensity dependence of the Langmuir–Hinshelwood kinetic parameter, k_{obs} , and that of the apparent adsorption parameter, K_R .
- To investigate on the interdependent influence of the concentration and light intensity on the photocatalytic degradation of metolachlor in water and butyric acid in air using $\text{TiO}_2/\text{SiO}_2$ coated on a non-woven paper in two different reactors.
- To discuss about the kinetic photocatalytic model based on the pseudo-steady-state approximation to have a better description and understanding of the experimental results.

The knowledge of this interdependence can be helpful to optimize the photocatalytic process. Especially if the model can

be transformed such as to lead to parameters that can be considered really constant.

2. Materials and methods

2.1. Chemicals

Technical grade metolachlor 97.9% was used for the experiments. Analytical-standard pesticide 98.4% was obtained from Riedel de Haën and used without further purification, for HPLC calibration. Analytical-grade organic solvents were used for HPLC-UV analysis. Analytical butyric acid 99% was purchased from Acros Organic and used without further purification. The water used in the experiments was obtained after purification through reverse osmosis (organic carbon = 0.2 mg L^{-1} , $\text{Cl}^- = 0.05 \text{ mg L}^{-1}$, $\text{NO}_3^- = 0.07 \text{ mg L}^{-1}$).

2.2. Photoreactors and light source

2.2.1. Liquid phase reactor

The irradiation of metolachlor solutions was carried out in a closed loop step photoreactor. This latter consists of several parts: a tank, a pump, a spillway at the top and steps. The reactor was made of six regular steps of the same dimensions (depth/height/width: $6 \text{ cm}/6 \text{ cm}/25 \text{ cm}$) covered with the photocatalytic media (0.18 m^2 ; $72 \text{ cm} \times 25 \text{ cm}$ corresponding to 4 g of TiO_2). Three UV lamps, Phillips PL-L24W/10/4P ($\lambda_{\text{max}} = 365 \text{ nm}$) were placed at the inside of a cover, the incident photon flux was measured by actinometry at $14.5 \pm 0.2 \text{ W m}^{-2}$ (one lamp); $27 \pm 0.2 \text{ W m}^{-2}$ (two lamps); $38 \pm 0.2 \text{ W m}^{-2}$ (three lamps) at the surface of the liquid. A sketch of the step photoreactor is given in Fig. 1a. In a typical experiment, 5.5 L of pesticide solution of various concentrations were introduced into the system. The solution was introduced at the beginning of the experiment into a tank equipped with a magnetic stirrer. The solution was pumped into the tank at a flow rate of 120 L h^{-1} . Samples were taken into the tank to evaluate the concentration of the target compound versus time. The liquid flow, on the photocatalytic media was a thin falling film with a thickness of about 1 mm . After adsorption equilibrium was reached in the dark, the UV light was turned on to irradiate the solution and the first sample was taken ($t = 0$).

2.2.2. Gas phase reactor

The photodegradation of butyric acid was carried out in a coaxial photoreactor (0.0216 m^3) which was made up of three independent parts: (1) a mobile central pierced cylinder supporting a catalytic filter ($5.67 \times 10^{-2} \text{ m}^2$) on its outside wall, (2) a fixed intermediate crown allowing to hold UV lamps, and (3) a mobile external envelope supporting a catalytic filter ($30.43 \times 10^{-2} \text{ m}^2$) on its internal wall (Fig. 1b). The reactor was made in stainless steel and the airtightness was assured by chemical resistant joints. Polluted effluent was introduced in the reactor by 12 injectors located on the top of the external envelope, and left the reactor through the center of the internal cylinder so that the flow undergoes tangential and transversal contacts. Moreover, turbulences and homogeneous irradiation were generated by inversely rotations of central and external cylinders around the reactor vertical axe. The gas flow rate was $1.5 \text{ m}^3 \text{ h}^{-1}$. Illumination was provided by 12 independent fluorescent tubes with a maximum intensity at 365 nm (Phillips TLD 15W/05). The photon flow ranged between 7 and 14 W m^{-2} . It was deduced from tracer analysis, that the reactor was a continuous perfectly mixed reactor.

2.2.3. Photocatalyst characteristics

The powdered photocatalyst was PC-500 Titania from Millennium Inorganic Chemicals (anatase $>99\%$; specific surface area $>320 \text{ m}^2 \text{ g}^{-1}$; crystallite mean size: $5\text{--}10 \text{ nm}$, characteristics from Millenium Chemicals company). Titania PC-500 was also coated on non-woven paper (natural cellulose fiber, 2 mm thick) using a binder. The binder was an aqueous dispersion of colloidal SiO_2 . The cellulose fiber was coated by a mixture of TiO_2 and SiO_2 ($\text{TiO}_2/\text{SiO}_2$ mass ratio: 1) using a size press. The TiO_2 surface load was 20 g m^{-2} after washing. In this study, the combination cellulose fiber/ $\text{TiO}_2/\text{SiO}_2$ will be referred to as the photocatalytic material.

2.3. Analyses

2.3.1. Liquid phase experiments

In a typical experiment, at scheduled times, 25 mL samples were taken from the reactor and filtered through a Millipore filter ($0.45 \mu\text{m}$) to avoid particles entering the instruments. The

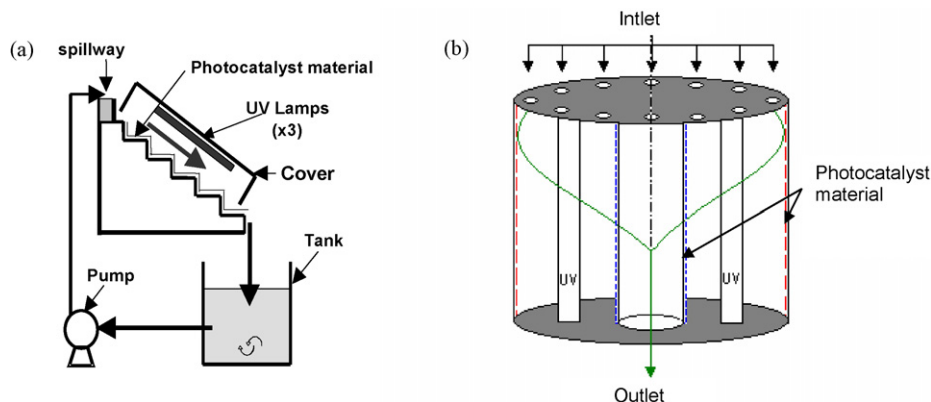


Fig. 1. (a) Step photoreactor for photocatalytic degradation in liquid phase. (b) Continuous photoreactor for photocatalytic degradation in gas phase.

concentration of pesticide was measured with HPLC system consisting of a gradient pump, WATERS 600 controller, an automatic injector WATERS 717 Plus and a diode array detector WATERS 996. Separation was performed by a WATERS C₁₈ symmetry column (4.6 mm × 250 mm) and an acetonitrile/water mixture (50%/50%) as the mobile phase. Flow rate was set at 1 mL min⁻¹. The radiant flux of the lamp was measured by means of a chemical actinometer. We used potassium ferrioxalate (K₃Fe(C₂O₄)₃·3H₂O) because its quantum yield remains quite constant between 250 and 400 nm, so its use could be extended to a polychromatic lamp. The actinometer was irradiated under conditions similar to those used during the study.

2.3.2. Gas phase experiments

The UV power reaching the photocatalyst surface was measured with a radiometric probe at 365 nm (VLX-3W/CX 365). Gas samples of butyric acid were taken with an airtight syringe and injected into gas phase chromatograph equipped with a flame ionization detector (Fisons GC9000). Separation was performed by a Chrompack FFAP-CB column (25 m × 0.32 mm) and nitrogen gas as the mobile phase.

3. Results

3.1. Photocatalytic degradation of metolachlor in water

In order to study the influence of the photonic flux and the concentration of the organic compound on the initial degradation rate, experiments were carried out with different photon flows and initial concentrations. Fig. 2a shows the influence of the light intensity on the initial degradation rate for different concentrations of metolachlor, i.e. before the formation of any by-products that might compete with the target compound for the adsorption sites. The initial degradation rate increases with increasing photon flux until a value from which the rate is independent of the photon flux and reaches a plateau. Ollis et al. [14] and D'Oliveira et al. [20] described the transformation of the order 1 of the reaction with regard to the intensity to an order of 1/2 which could be explained by the recombination of the electron-hole. Accordingly, below a given I value the formation of the electron-hole is limiting and above this value the reaction between the oxidant species and the metolachlor becomes limiting. However, in our results, the changes in the kinetic order relative to the light intensity do not occur for the same I value. It appears to be dependent on the concentration (Fig. 2a). As an example, for the concentration of metolachlor $C_0 = 0.025$ mM, the order reaction kinetic with respect to I appears to be already 0 for all the photon fluxes used, whereas for a concentration of $C_0 = 0.4$ mM, this order is about 0 only for the highest light intensity (38 W m⁻²).

The previous results can be represented in a different way as in Fig. 3a where the initial degradation rate versus initial concentration is shown for three different photon fluxes. Fig. 3a clearly shows that the changes of kinetic order relative to the concentration do depend on the value of I . Indeed, for the

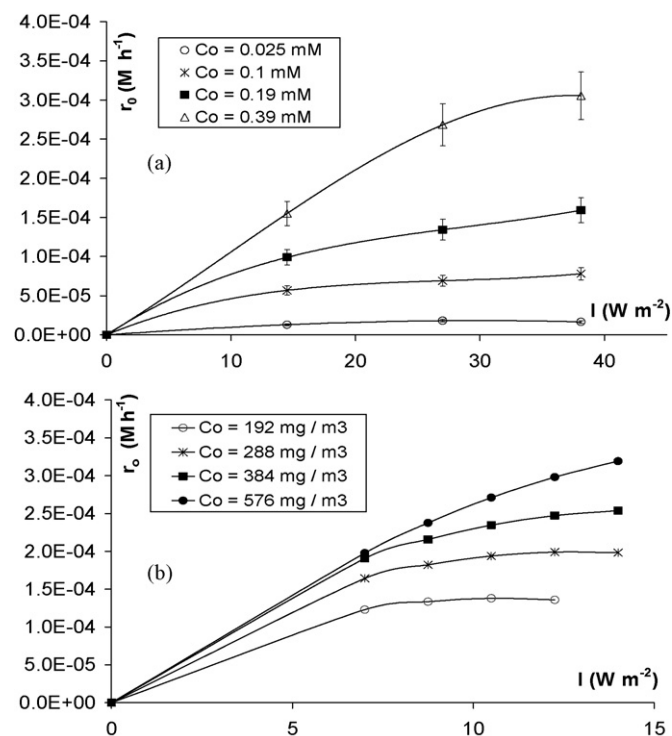


Fig. 2. Initial degradation rate as a function photon flux for different initial concentrations of metolachlor in liquid phase (a) and butyric acid in gas phase (b). In liquid phase the value C_0 is the concentration at the equilibrium after dark adsorption.

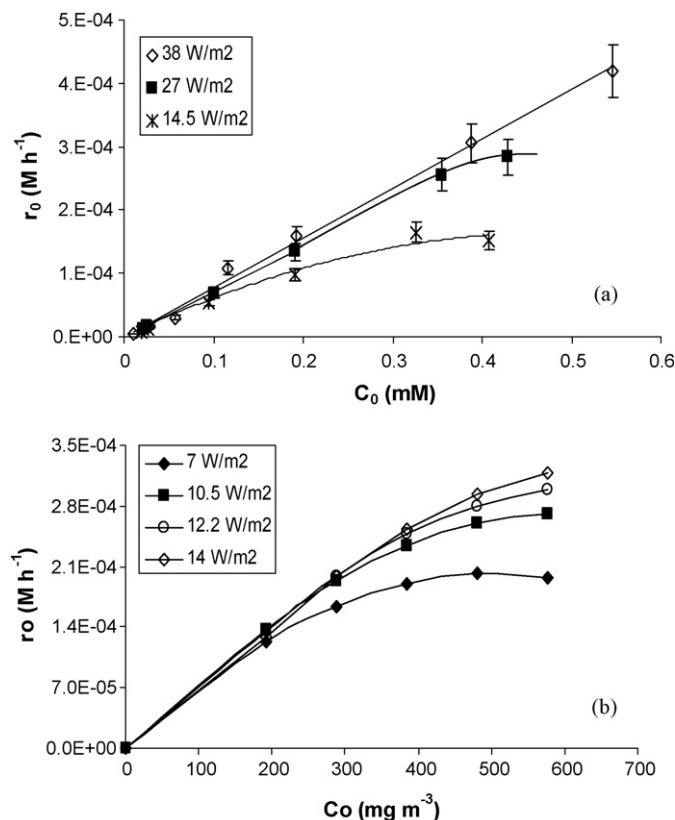


Fig. 3. Initial degradation rate as a function of initial concentration of metolachlor in liquid phase (a) and butyric acid in gas phase (b).

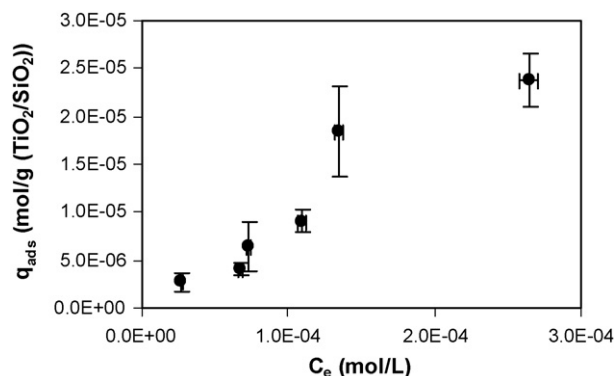


Fig. 4. Adsorption isotherm of metolachlor on $\text{TiO}_2/\text{SiO}_2$ coated medium in liquid phase. $T = 25^\circ\text{C}$.

experiments carried out with a photon flux of 14.5 W m^{-2} the initial rate reaches a plateau for a value of the concentration $C_0 = 0.3\text{ mM}$ whereas for the experiments with a photon flux of 38 W m^{-2} the plateau has not been reached in the range of the studied concentrations (C_0 up to 0.55 mM). The interdependence of the initial degradation rate towards the initial concentration and the photon flux has been described, as far as we know, only by [16] with a suspension of TiO_2 and is confirmed, in this present work, for a fixed TiO_2 , in liquid phase. Fig. 4 shows the adsorption isotherm of metolachlor on $\text{TiO}_2/\text{SiO}_2$ coated paper.

3.2. Photocatalytic degradation of butyric acid in air

Following the same experimental strategy, experiments were carried out with the second setup. Light intensities, concentrations and rates are of course different but Figs. 2b and 3b show clearly the same aspect: the order of the initial degradation rate with regard to I depends on the initial concentration of butyric acid and the order with regard to C_R depends on the light intensity.

This experimental evidence, observed for the first time in the gas phase, confirms those observed in water.

4. Discussions

Following the method proposed by Emeline et al. [16], initial photocatalytic degradation rates were approximated by L-H expression (1a) for both phases, the value of the kinetic parameter, k_{obs} , and the apparent adsorption parameter K_R are plotted in Fig. 5a (liquid) and b (gas). The results clearly show that both parameters are functions of light intensity: The L-H model parameters, k_{obs} , and $1/K_R$, depend linearly on photon flow.

As invoked by Ollis [19], the dependence of the apparent adsorption parameter with respect to I makes flaws in the L-H slow step photocatalysis model. In the Langmuir isotherm form (5), the dark adsorption equilibrium constant should not depend on photon flow since $K(\text{dark}) = k_1/k_{-1}$. The dependence of the apparent adsorption parameter with intensity was also reported for the photocatalytic degradation of phenol [16] and acetophenone [17] in liquid phase.

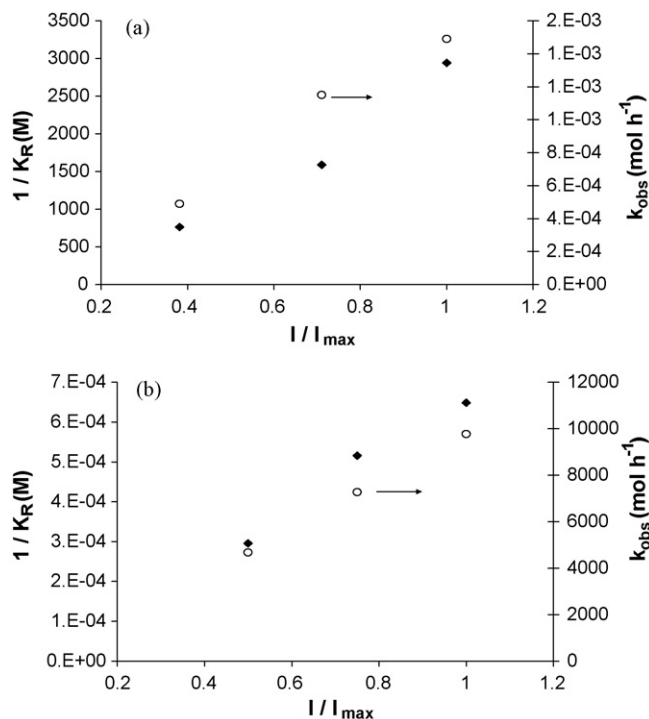


Fig. 5. Influence of the photon flow on parameter k_{obs} and K_R of the L-H model in liquid phase (a) and gas phase (b).

This is the first experimental evidence that the kinetic parameter and the apparent equilibrium parameter are functions of the photon flow in gas phase. Thus, the results observed in liquid phase are confirmed and can be generalized for a fixed TiO_2 .

The value of K_R is found to be larger than the value of $K(\text{dark})$ in accordance with other research groups [21–23]. Based upon those results and in accordance with Ollis [19] and Emeline et al. [16] the apparent adsorption parameter in L-H model cannot be considered just as an adsorption equilibrium constant.

In our previous works [11,12] we showed the influence of the concentration of the dissolved oxygen concentration in water and proposed a method to calculate the adsorption constant of oxygen on TiO_2 . Herein we will consider the dissolved oxygen concentration constant, in accordance with experimental measurements and in order to simplify the development of the models.

During the photocatalytic process, the electron/hole pairs are generated by a photoexcitation within the spectral range of 300–400 nm, where the production of charge-carriers (e^- ; h^+) is proportional to the photon flow (8):

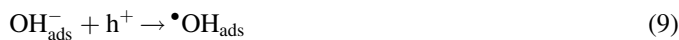


During the photocatalytic degradation of organic compounds in water, it is widely accepted that the $\bullet\text{OH}$ radicals are the main oxidative species [10,24]. The presence of the $\bullet\text{OH}$ radicals during irradiation of TiO_2 in water has been shown with electron spin resonance apparatus [25].

4.1. Kinetic models

4.1.1. Production of $\bullet\text{OH}$ radicals

The surface OH^- groups and/or adsorbed water trap the surface holes and form $\bullet\text{OH}$ radicals [12]:

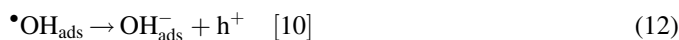


The rate expression for the formation of the $\bullet\text{OH}$ radicals is given by:

$$r_p = k_p[\text{OH}_{\text{ads}}^-][h^+] \quad (11)$$

4.1.2. Deactivation of the hydroxyl radicals

The hydroxyl radical species can be deactivated by detrapping of holes or via a reaction with surface electrons, [10,16].



Emeline et al. [16] proposed to consider the recombination of $\bullet\text{OH}$ radicals with surface electrons as the major pathway to explain the interdependence of the reaction rate with photon flow and the concentration of the target compound. Herein, we will consider that recombination may occur through both processes. If one or the other might be neglected, it should appear when fitting the model to the experimental results.

The kinetic expressions of the deactivation of the $\bullet\text{OH}$ radicals, respectively, associated with reactions (12) and (13) are:

$$r_{d1} = k_{d1}[\bullet\text{OH}_{\text{ads}}] \quad (14)$$

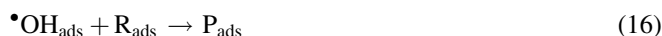
and

$$r_{d2} = k_{d2}[\bullet\text{OH}_{\text{ads}}][e^-] \quad (15)$$

4.1.3. Reaction with organic compounds

Based upon the assumption that the hydroxyl radicals are the main oxidative species during photocatalytic degradation, three pathways for the oxidation of the organic compounds R can be proposed [10]:

- A reaction occurring between the $\bullet\text{OH}$ radicals at the surface of the catalyst and the adsorbed molecule R (Langmuir–Hinshelwood mechanism):



- A reaction occurring between the $\bullet\text{OH}$ at the surface of the catalyst and the compound R in the solution (Eley–Rideal mechanism (E-R)):



- A reaction occurring between the $\bullet\text{OH}$ in solution and the compound R in the solution.

For the three pathways, the general kinetic expression of the compound degradation is:

$$r = k_r[\bullet\text{OH}]C_R \quad (18)$$

with $\bullet\text{OH}$ and R adsorbed on the catalyst or in the solution, according to each situation.

4.1.4. Expression of the hydroxyl radical concentration with pseudo-steady-state approximation

Assuming a quasi-steady-state, the formation rate of $\bullet\text{OH}$ radicals is given by:

$$\begin{aligned} r_{\bullet\text{OH}} &= k_p[\text{OH}_{\text{ads}}^-][h^+] - k_r[\bullet\text{OH}]C_R - k_{d1}[\bullet\text{OH}_{\text{ads}}] \\ &\quad - k_{d2}[\bullet\text{OH}_{\text{ads}}][e^-] \\ &\approx 0 \end{aligned} \quad (19)$$

Turchi and Ollis [10] have demonstrated that a diffusion of $\bullet\text{OH}$ in solution is not possible, thereby eliminating the third pathway. So Eq. (19) should be written considering that the hydroxyl radical are adsorbed and react with organic compound:

$$r = k_r[\bullet\text{OH}_{\text{ads}}]C_R \quad (20)$$

where C_R is the concentration of the reagent in the solution or adsorbed, this point will be discussed further later on.

As a consequence, the concentration of the $[\bullet\text{OH}_{\text{ads}}]_0$ for a single compound before any significant amount of by-products can be obtained, by using expression (19), as follow:

$$[\bullet\text{OH}_{\text{ads}}]_0 = \frac{k_p[\text{OH}_{\text{ads}}^-][h^+]}{k_rC_R + k_{d1} + k_{d2}[e^-]} \quad (21)$$

The $[e^-]$ and $[h^+]$ concentrations depend on the photonic flux absorbed by the TiO_2 , thus $[e^-]$ and $[h^+]$ are proportional to I , with a coefficient α , therefore expression (21) becomes:

$$[\bullet\text{OH}_{\text{ads}}]_0 = \frac{k_p\alpha[\text{OH}_{\text{ads}}^-]I}{k_rC_R + k_{d1} + k_{d2}\alpha I} \quad (22)$$

Expression (22) of the hydroxyl radical is similar to those reported by [10,16]. For a constant pH of the solution, Eq. (22) can be reduced to:

$$[\bullet\text{OH}_{\text{ads}}]_0 = \frac{k'_p I}{k_rC_R + k_{d1} + k'_{d2} I} \quad (23)$$

where $k'_p = k_p\alpha[\text{OH}_{\text{ads}}^-]$ and $k'_{d2} = k_{d2}\alpha$.

Two pathways can still be considered for the reaction of $\bullet\text{OH}$ with the organic compound, the E-R and L-H mechanisms.

4.1.5. Eley–Rideal mechanism

Assuming an Eley–Rideal mechanism for the reaction of the organic compound and the hydroxyl radical, i.e. dissolved organic compound reacts with adsorbed $\bullet\text{OH}$ radicals, the degradation rate expression should be:

$$r = k_{\text{rER}}[\bullet\text{OH}_{\text{ads}}]C_{\text{Rs}} \quad (24)$$

where C_{Rs} is the concentration of the compound in solution. Including expression (23) in expression (24), expres-

sion (25) is obtained:

$$r_0 = \frac{k_{\text{rER}} k_p' C_{\text{Rs}} I}{k_{\text{rER}} C_{\text{Rs}} + k_{\text{d1}} + k_{\text{d2}}' I} \quad (25)$$

Eq. (25) can be transformed into Eq. (1a) if

$$K_{\text{R}} = \frac{k_{\text{rER}}}{k_{\text{d1}} + k_{\text{d2}}' I} \quad (26)$$

and

$$k_{\text{obs}} = k_p' I \quad (27)$$

Hence $1/K_{\text{R}}$ should be proportional to I , when $k_{\text{d1}} \ll k_{\text{d2}}' I$, and k_{obs} should be proportional to I . So, Eq. (25) refers to all the experimental dependencies of the apparent equilibrium constant and rate constant with regard to the light intensity report in the present work in liquid and gas phase and confirmed results of others research groups [16,17].

4.1.6. Langmuir–Hinshelwood mechanism

Assuming an L-H mechanism for the reaction of the organic compound and the hydroxyl radical, i.e. adsorbed organic compound reacts with adsorbed $\bullet\text{OH}$ radicals, the degradation rate expression is

$$r = k_{\text{rLH}} [\bullet\text{OH}_{\text{ads}}] C_{\text{Rads}} \quad (28)$$

The concentration of the adsorbed organic compound (C_{Rads}) is given by the Langmuir equation (29):

$$C_{\text{Rads}} = \frac{C_{\text{Rads0}} K C_{\text{Rs}}}{1 + K C_{\text{Rs}}} \quad (29)$$

where C_{Rads0} is the maximum coverage. Including expressions (23) and (29) in Eq. (28), expression (30) is obtained:

$$r = \frac{k_{\text{rLH}} k_p' C_{\text{Rads0}} K C_{\text{Rs}} I}{(k_{\text{rLH}} C_{\text{Rads0}} + k_{\text{d1}} + k_{\text{d2}}' I) K C_{\text{Rs}} + k_{\text{d1}} + k_{\text{d2}}' I} \quad (30)$$

Eq. (30) can be transformed into Eq. (1a) if

$$K_{\text{R}} = \frac{(k_{\text{rLH}} C_{\text{Rads0}} + k_{\text{d1}} + k_{\text{d2}}' I) K}{k_{\text{d1}} + k_{\text{d2}}' I} \quad (31)$$

and

$$k_{\text{obs}} = \frac{k_{\text{rLH}} k_p' C_{\text{Rads0}} I}{k_{\text{rLH}} C_{\text{Rads0}} + k_{\text{d1}} + k_{\text{d2}}' I} \quad (32)$$

k_{obs} is not completely proportional to I and can only describe our experimental results if we consider that the $\bullet\text{OH}$ radicals react with adsorbed molecules faster than they recombine with hole and surface electrons, that is $k_{\text{r}} C_{\text{Rads0}} \gg k_{\text{d1}} + k_{\text{d2}}' I$.

Then expressions (31) and (32) could be transformed into expressions (33) and (34):

$$K_{\text{R}} = \frac{k_{\text{rLH}} C_{\text{Rads0}} K}{k_{\text{d1}} + k_{\text{d2}}' I} \quad (33)$$

$$k_{\text{obs}} = k_p' I \quad (34)$$

$1/K_{\text{R}}$ becomes again proportional to I when $k_{\text{d1}} \ll k_{\text{d2}}' I$, and k_{obs} proportional to I , in accordance with our experimental results.

Emeline et al. [16] make the same assumption, i.e. the slower recombination with surface electron, and suggest that it is caused by “a slower rate of electron transport from the bulk to the surface because of an accumulation of negative charges on the photocatalyst surface”. In the present study, the TiO_2 particles are deposited using a SiO_2 binder [26] with a pH of zero charge, pH_{ZC} , which is lower than the TiO_2 ($\text{pH}_{\text{ZC}}(\text{SiO}_2) = 2.5$; $\text{pH}_{\text{ZC}}(\text{TiO}_2) = 6.2$). At the experimental pH (metolachlor in water, pH 7.2), the silica binder is mainly charged negatively (SiO^-) [27] so the corresponding negative electric field can diminish the rate of electron transport and would support the assumption of a slower recombination with surface electron. Unfortunately this assumption cannot be used for the gas phase where the notion of pH is not relevant.

4.2. Correlation to describe the experimental interdependence

The kinetic study based upon the L-H and E-R model shows that both models can be used to explain the interdependence of initial degradation rate with regard to the initial concentration and photon flow. The use of a correlation where the model parameters are independent of the initial concentration and light intensity, i.e. really constant, is required to perform reliable and detailed simulations of existing reactors and future designs.

The first model fitting trials have been performed with model (6) with success for gas phase but when applied to liquid phase, the fit does not satisfactorily describe the experimental results (Fig. 6 and Table 1). Based on the previous developments; we will investigate another correlation able to take into account the experimental interdependence observed. As will be shown, below, the two approaches can be reduced to the same form of correlation.

4.2.1. Eley–Rideal mechanism

The initial degradation rate is described by expression (25):

$$r_0 = \frac{k_{\text{rER}} k_p' C_{\text{Rs}} I}{k_{\text{rER}} C_{\text{Rs}} + k_{\text{d1}} + k_{\text{d2}}' I} \quad (25)$$

by dividing the numerator and the denominator by k_{d1} , the following expression is found:

$$r_0 = \frac{k_{\text{rER}} k_p' / k_{\text{d1}} I}{((k_{\text{d2}}' / k_{\text{d1}}) I) + 1 + ((k_{\text{rER}} / k_{\text{d1}}) C_{\text{Rs}})} C_{\text{Rs}} \quad (35)$$

Finally, the initial degradation rate expression is given:

$$r_0 = \frac{\beta I}{1 + \gamma I + \chi C_{\text{Rs}}} C_{\text{Rs}} \quad (36)$$

where $\beta = k_{\text{rER}} k_p' / k_{\text{d1}}$, $\gamma = k_{\text{d2}}' / k_{\text{d1}}$, $\chi = k_{\text{rER}} / k_{\text{d1}}$. These parameters should be independent of the photon intensity and the initial concentration of the compound. In Eq. (36) for a given concentration, for high light intensities, when $\gamma I \gg 1 + \chi C_{\text{R}}$, the reaction order becomes 0 with regard to light intensity.

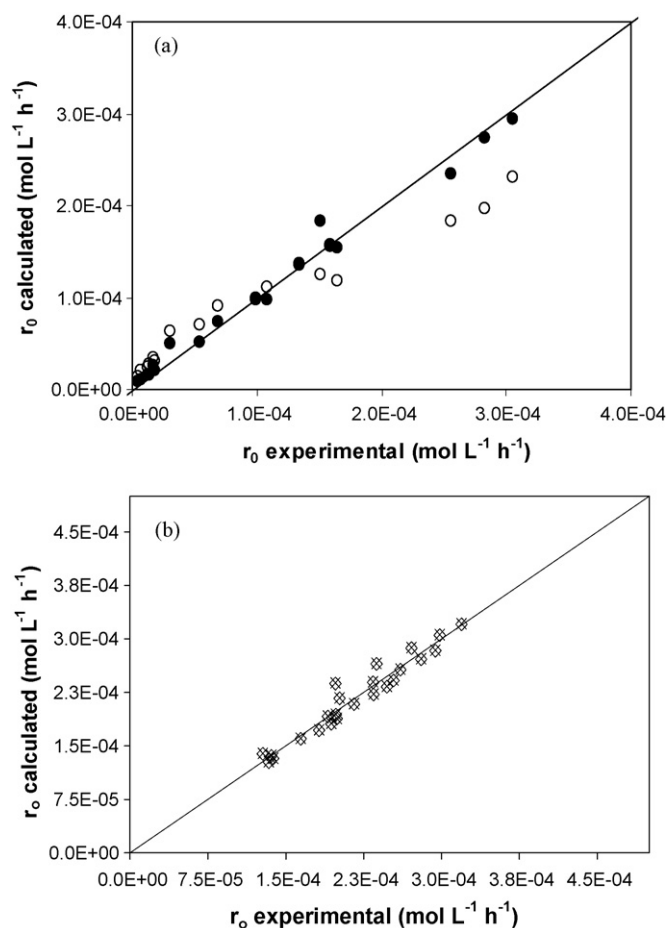


Fig. 6. Diagram of dispersion for the comparison of the experimental initial degradation rate and the rate calculated according to Eq. (36) (●; ◇) and Eq. (6) (○; ×) for metolachlor in solution (a) and butyric acid (b).

Similarly, for a given photon flow, for high concentrations, when $\chi C_R \gg 1 + \gamma I$, the reaction order is 0 with regard to initial concentration.

4.2.2. Langmuir–Hinshelwood mechanism

The expression of the initial degradation rate using Eqs. (33) and (34) is:

$$r = \frac{k_{rLH} k'_p C_{\text{Radso}} K C_{\text{Rs}} I}{k_{rLH} C_{\text{Radso}} K C_{\text{Rs}} + k_{d1} + k'_{d2} I} \quad (37)$$

by dividing the numerator and the denominator by k_{d1} , the following expression is found:

$$r = \frac{(k_{rLH} k'_p C_{\text{Radso}} K / k_{d1}) I}{((k_{rLH} C_{\text{Radso}} K / k_{d1}) C_{\text{Rs}}) + 1 + ((k'_{d2} / k_{d1}) I)} C_{\text{Rs}}$$

Finally the degradation rate expression is given:

$$r_0 = \frac{\beta' I}{1 + \gamma' I + \chi' C_{\text{Rs}}} C_{\text{Rs}} \quad (38)$$

Table 1

Values of the constants for the two correlations ((6); (24)) and level of significance associated δ

Model	Parameter	Gas phase	Liquid phase
$r_0 = \frac{\alpha I C_R}{\beta I + \gamma C_R}$	β / χ	0.13	0.031
	γ' / χ	580	0.024
	δ	5×10^{-31}	5×10^{-14}
	r^2	0.996	0.959
$r_0 = \frac{\beta I}{1 + \gamma' I + \chi' C_{\text{Rs}}} C_{\text{Rs}}$	β (L Ein^{-1})	2.83×10^6	199
	γ (h L Ein^{-1})	3.76×10^4	156
	χ (L mol^{-1})	2.18×10^7	1225
	δ	5×10^{-31}	3×10^{-22}
	r^2	0.996	0.995

The calculations were carried out on 19 and 24 experimental points in liquid and gas phases, respectively.

where

$$\begin{aligned} \beta' &= \frac{k_{rLH} k'_p C_{\text{Radso}} K}{k_{d1}} = \frac{k_{rLH} C_{\text{Radso}} K}{k_{rER}} \beta \\ \gamma' &= \frac{k'_{d2}}{k_{d1}} = \gamma \\ \chi' &= \frac{k_{rLH} C_{\text{Radso}} K}{k_{d1}} = \frac{k_{rLH} C_{\text{Radso}} K}{k_{rER}} \chi \end{aligned} \quad (39)$$

These parameters should again be independent of the photon intensity and the initial concentration of the compound.

It has to be mentioned that the value of the constants β , γ and χ , or β' , γ' and χ' , respectively, are calculated for a given dissolved oxygen concentration. According to the previous developments and Eq. (1), only β (and β') should be affected:

$$\beta = \beta_2 \frac{K_{\text{O}_2} C_{\text{O}_2}}{1 + K_{\text{O}_2} C_{\text{O}_2}} \quad (40)$$

For Eq. (6) the values of β / χ and γ / χ are given because this correlation is over defined. The values of β , γ and χ or β' , γ' and χ' were fitted using a relative least square method. The diagram of dispersion of the experimental versus calculated initial rate is represented in Fig. 6. A test of significance for the Pearson correlation coefficient (r^2) [28] has been performed on the gas and liquid phase experiments. The values of the level of significance (δ) in each case indicate that there is a strong significant correlation between the experimental initial rate and the fitted models based on relation (24) or (6) (Table 1). There is clear evidence that the correlation is valid and confirms the interdependence of the rate with respect to intensity and concentration. Nevertheless, the residual, for the liquid case, for Eq. (6), exhibits a non-random dispersion versus the initial rate degradation (Fig. 6a). For our correlation (24), in liquid phase, the fit is much better. Eq (6) can be regarded as the rate equation when it is considered that the $\bullet\text{OH}$ radicals react only with target compound (Eq. (18)) and the free electron (Eq. (13)). While Eqs. (36) and (38) include, in addition, a reaction depending solely on the hydroxyl radicals concentration (Eq. (12)). It appears that the value: $\gamma I + \chi C_{\text{Rs}}$, in the denominator, ranges from 0.8 to 2.8. The value “1” in the denominator

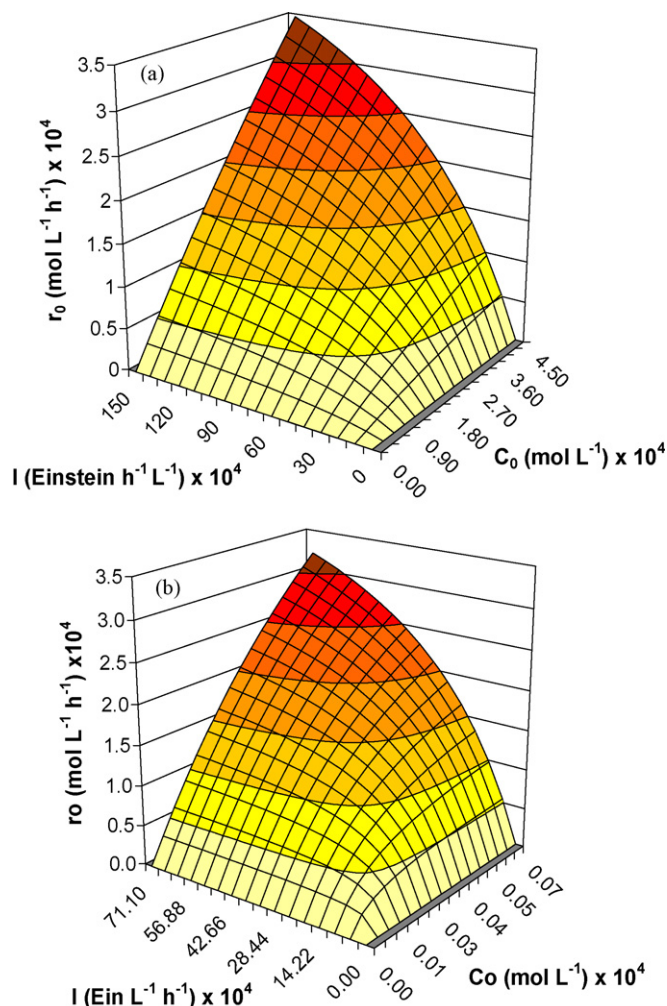


Fig. 7. Modeling of the initial degradation rate of metolachlor (a) and butyric acid (b) as a function of the initial concentration and the photon flow.

can therefore not be neglected. For the gas phase degradation, the value of β , γ , χ are very important and $\gamma I + \chi C_{Rs} \gg 1$, thus Eq. (24) reduces almost into Eq. (6). The calculated dependence of the degradation rate of metolachlor and butyric acid by photocatalysis on both photon flux and pollutant concentration is presented in Fig. 7.

The good fit obtained for the two systems, gas phase photocatalysis and liquid phase photocatalysis, clearly indicates that this form of model defines more closely the real trend of the photocatalytic process. However, it does not allow discriminating between the Eley–Rideal and the Langmuir–Hinshelwood approaches. The only way to discriminate the models at this stage would be to have a closer look at χ and χ' . According to Eq. (30), i.e. before the additional assumption relative to the electron–hole pair recombination, χ' should be a linear function of I , whereas χ should be a real constant. Either the assumption is true and we still cannot discriminate, or the assumption is weak and a more detailed analysis of χ' might give us a hint. Unfortunately, the data collected for this study is not rich enough, additional experimentation are needed.

Further model development and experimental work should be carried out to provide a rigorous model, based on the values of the real constants k_{d1} , k_{d2} , k_p , etc., able to describe the experimental interdependence observed in this present work.

5. Conclusion

Experimental photocatalytic degradation of metolachlor in water and butyric acid in air showed that change of kinetic order with respect to light intensity depend on the initial concentration value of the target compound and reversely. The apparent adsorption parameter, K_R , from the L-H model varies with the light intensity both in liquid and gas phases and thus cannot be considered as a Langmuir constant. A kinetic approach using pseudo-steady-state for the concentration of $\bullet\text{OH}$ radical associated either with E-R or L-H models makes consistent the interdependence of the degradation rate with initial concentration and photon flow under certain assumptions. For the two models, it has been assumed that $\bullet\text{OH}$ radicals recombine both with e^- and h^+ . Both models have the same form if an additional assumption is made for the L-H model, it had to be proposed that recombination with surface e^- is slower than the reaction with target compound. A correlation was used to describe the experimental interdependency. The constants used in this correlation are independent of the initial concentration of the organic compound and light intensity. The present paper highlights the importance of the interdependence on the concentration and the light intensity of photocatalytic degradation rate. The optimal conditions are reached when the photocatalytic degradation rate is linear with the photon flow, since photon flow is not “wasted” in these conditions. In accordance with our results it can be stated that there is an optimal photon flow for a given initial concentration. Hence, to have a better energetic balance, when electric UV lamp are used, it could be proposed to reduce the photon flow in the course of the reaction (or mineralization) to always keep a kinetic order of one in regard with light intensity. So it would be carried out “photocatalytic degradation at varying light intensity”.

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